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Determination of the Diamagnetic Anisotropy of the Nematic Phase of p-Methoxybenzylidene-p-n-butylaniline (MBBA)†

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A nuclear magnetic resonance method is used to obtain values of the volume diamagnetic anisotropy of MBBA from 274°K to 318°K. The anisotropy change from 0.169 to 0.074×10^{-6} over this temperature range is discussed in terms of the order parameter, S. It is estimated that S is ~ 0.3 at the clearing point.

INTRODUCTION

One of the earliest techniques used in the study of nematic liquid crystals was measurement of the diamagnetic susceptibility.[1] The change of susceptibility with temperature can be significant for the nematic phase. It occurs owing to varying amounts of order achieved in the nematic state by molecules that generally possess a fairly large anisotropy in the principal components of the susceptibility.[2]

[†] Presented at the Fourth International Liquid Crystal Conference in Kent, Ohio, August, 1972.

Since a substantial degree of order is a principal characteristic of nematic liquid crystals, a knowledge of the magnitude of this property is of major significance in efforts to attain an understanding of the nematic state. In addition, a knowledge of the diamagnetic anisotropy, *per se*, is required in determinations of the elastic constants of a nematic fluid and, in general, to understand magnetic-field effects.[3]

The compound, *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA), has a nematic phase that has been the subject of many recent studies. The present study was made to determine the diamagnetic susceptibility and anisotropy for MBBA as a function of temperature in the nematic range. The measurements were made by a nuclear magnetic resonance (NMR) method.

EXPERIMENTAL

Measurements were made with a Varian HA-100 spectrometer operating at 100 MHz and a field intensity of 23.4 kG. Frequency sweeps were done by scanning an audio-frequency sideband synchronized with the recorder-pen movement; however, no field-frequency lock was employed. Drift was electronically minimized, and each reported measurement is an average of at least six scans in each direction. The variable-temperature probe permitted temperature control to within 0.1°C; however, the actual temperatures are known only to ± 0.3°C. Temperature was measured frequently using calibration curves[4] for the chemical shifts of methanol and ethylene glycol samples supplied by Varian Associates.

The volume susceptibility, κ, of the MBBA was measured by the (nonspinning) coaxial sample tube NMR method.[5,6] The inner cylinder contains the MBBA sample and the annular region of the cell contains an arbitrary liquid that produces a proton NMR signal. This signal, referred to as the "reference," has the appearance of a doublet with a splitting, $\Delta H/H_0$, given by:[5,6]

$$\Delta H/H_0 = A\kappa_\mu + B\kappa_r + C \tag{1}$$

where κ_μ and κ_r are the unknown (MBBA) and reference liquid susceptibilities, and A, B, and C are cell constants. Bernheim and Krugh[7] recently suggested this method for measuring the diamagnetic *anisotropies*, $\Delta\kappa$, of nematic liquid crystals. Following their approach, we measure the splitting $\Delta H_{\text{nem}}/H_0$ when MBBA is nematic ($\kappa_\parallel$) and $\Delta H_{\text{iso}}/H_0$ when it is isotropic. It is easy to show that these are related to the anisotropy of volume susceptibility, $\Delta\kappa$, in the following equation:

$$\Delta\kappa = -\frac{3}{8\pi k_1^2}\left[\frac{\Delta H_{\text{iso}} - \Delta H_{\text{nem}}}{H_0}\right] \tag{2}$$

where H_0 is the applied magnetic field and k_1 is a cell constant. Actually, Eq. (2) ignores the variations in liquid densities, which are an important consideration in this study and are discussed in a later section. We also note that Eq. (2), as given in Ref. 7, incorrectly omits the negative sign.[†]

A set of precision glass coaxial sample tubes from Wilmad Glass Company, Inc., were used. These gave $k_1{}^2 = 1.832$. Based on experiments done on a number of liquids with known susceptibility, the uncertainty in measurements of κ by this method should be less than one percent.

The MBBA sample used in our measurements had been recently redistilled; the nematic–isotropic transition, T_c, was 45.5-46°C. The transition temperature was determined using a heating rate of ~ 2°C/h in the vicinity of the transition. This determination was made on the actual NMR sample both before and after the magnetic measurements. A drop in T_c of $\lesssim 0.5$°C occurred for this sample after about a week in a tube closed with a snug polyethylene cap and several layers of paraffin film. (After 8–10 weeks, the transition temperature dropped several degrees.)

Density measurements on MBBA were made at temperatures above 25°C by weighing the MBBA contained in a small pycnometer that consisted of a bulb blown at the end of a capillary tube. Constant volume of liquid was obtained at each temperature by blotting away the excess. The volume was calibrated at 25.0 and 40.0°C with distilled H_2O. The densities reported are estimated as accurate to ± 0.0002 g/cm^3. The temperature dependence of the 1,4-dioxane density was measured by a dilatometric method which gave an estimated uncertainty of $\leqslant \pm 0.0010$ g/cm^3.

RESULTS

Susceptibility measurements from –4°C to +52°C were done on MBBA using an acetone reference and from +15°C to 84°C using a 1,4-dioxane reference. The limits were set by the freezing and boiling points of the reference liquids.

For temperatures higher than 46°C, the PMR spectrum includes numerous, intense resonances from the various protons of MBBA. These partially obscured the reference signal, though at lower temperatures, only the signal from the reference was observed. Heating to within about one degree of the clearing point (taken as 46.0°C) produced a PMR spectrum that contained very weak high-re-

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[†] The splitting, ΔH, may be either positive or negative depending upon the various susceptibilities of the cell components. The sign may be determined easily by observing the influence on the NMR signal of X or Z field gradients which can be produced intentionally by the spectrometer homogeneity controls.

solution signals from the MBBA, intensities of which remained constant at constant temperature for many hours. Within a range of a few tenths of a degree, the intensities of these peaks could be varied considerably. Then, discontinuous increase occurred when a temperature of $\simeq 46.0°C$ was reached. Increase of intensity above the isotropic transition temperature was observable but the rate of increase was much smaller than for $45 < T < 46°C$. Several representative spectra in the vicinity of the transition are shown in Figure 1.

The appearance of high-resolution signals in this range of temperature might be thought to be attributed to the motions of the molecules becoming, overall, more nearly isotropic. On the other hand, direct visual observation of the MBBA sample, while slowly increasing the temperature, indicates that in a temperature interval about 0.5° below the clearing point there coexist distinct nematic *and* isotropic regions. This situation can be observed to persist for long periods of time (over one hour) while the temperature of the bath is held constant to within ± 0.1°C. The NMR signals are presumed to arise from this equilibrium isotropic phase and, therefore, no susceptibility or anisotropy measurements were done in this interval.

At about −4°C, a discontinuous change in susceptibility was noted as the apparent limit of supercooling was reached and crystalization took place. Sub-

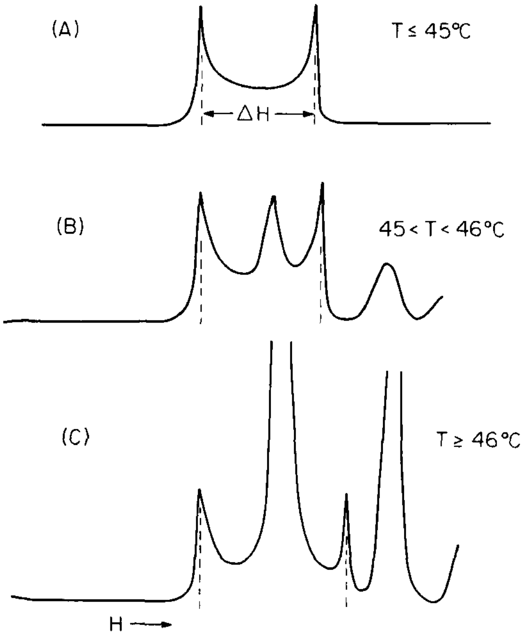

FIGURE 1. Typical spectra obtained from the concentric NMR sample cell containing MBBA and 1,4-dioxane at (A) $T \leqslant 45°C$, (B) $45° < T < 46°C$, (C) $T > 46°C$.

sequent heating of the solid MBBA resulted in a maximum in the volume susceptibility around 15°C followed by the solid-to-nematic transition, which appeared complete at 22.5°C. Specific volume data for the solid are not available; however, it appears from our data and those of a recent study[8] that MBBA forms an essentially unoriented microcrystalline solid when suddenly crystallized in the magnetic field. We obtained an unoriented solid phase even when the rate of MBBA crystal growth was greatly retarded by seeding the supercooled liquid at ~ 20°C in the magnetic field.

Figure 2 shows the values of the splitting, $\Delta H/H_0$, observed for the acetone and dioxane reference signals. The identical MBBA sample was used in each

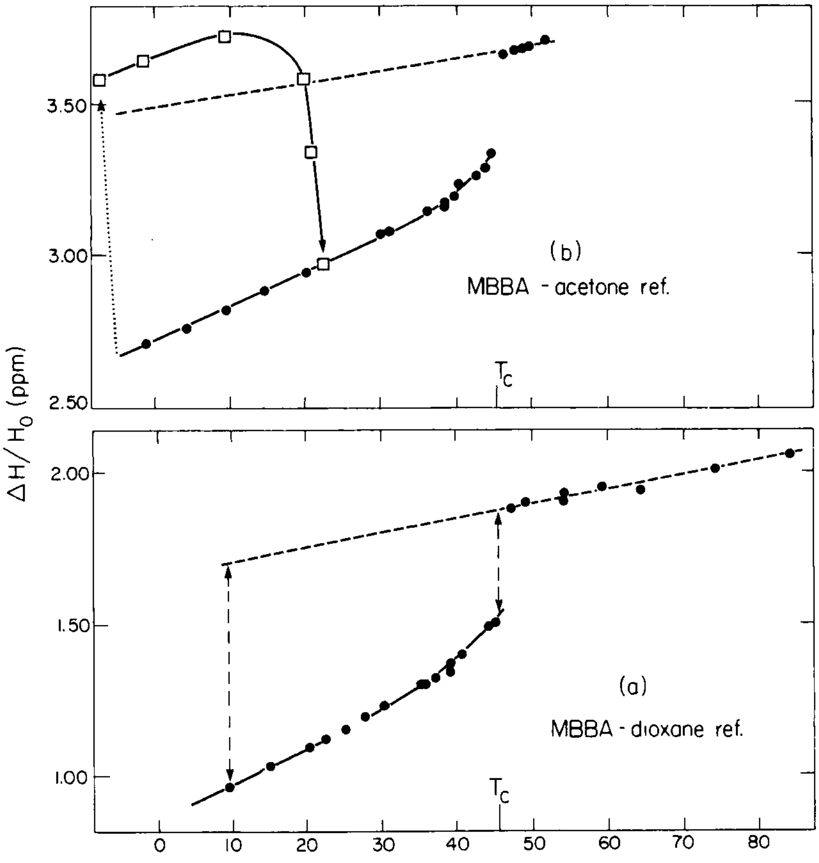

FIGURE 2. The observed variation of the splitting, $\Delta H/H_0$, given by the NMR signal of the reference liquid. (a) MBBA–dioxane. (b) MBBA–acetone; the values indicated by □ are for solid MBBA. The vertical lines indicate the manner in which $(\Delta H_{\text{nem}} - \Delta H_{\text{iso}})/H_0$ is obtained.

series, only the (outer) reference liquid being changed. Within the reproducibility of ± 0.01 ppm, both heating and cooling produced the same value of $\Delta H/H_0$.

The volume susceptibility of the isotropic MBBA fluid is also obtained from the PMR data, as well as $\kappa_{\parallel}$, the susceptibility of the nematic liquid along the magnetic-field direction. The absolute magnitude of κ for MBBA was consistently ~ 0.5–1.0% higher as determined with the dioxane reference, compared to the acetone reference. The origin of the discrepancy is most likely in the susceptibilities assumed for acetone (-0.460×10^{-6}, 20°C) and dioxane (-0.606×10^{-6}, 32°C) since the over-all, absolute accuracy of the NMR method is limited by such uncertainty. At 46°, κ is $-0.691 \pm .007 \times 10^{-6}$ for isotropic MBBA. The $\kappa_{\parallel}$ values are given in Table I and were taken from a smooth curve that was fitted to both experimental data sets. The anisotropy determinations do not depend upon any knowledge of the reference liquid susceptibility. The sensitivity of the anisotropy determination to errors in the measured $\Delta H/H_0$ values results in an estimated uncertainty of $\pm .008 \times 10^{-6}$.

Since it is of interest to know χ, the susceptibility *per unit mass*, as well as $\kappa (= \chi \rho)$, it is necessary to know the densities of the liquids (MBBA and reference) and their temperature coefficients, $d\rho/dT$. The value of $\rho\,(T)$ is particularly important to know in order to calculate anisotropy values from the NMR data.

TABLE I

The Diamagnetic Susceptibility and Anisotropy of MBBA as a Function of Reduced Temperature

T/T_c	$-\kappa_{\parallel} \times 10^6$ (cc^{-1})[a]	$\Delta\kappa_m \times 10^6$ (cm^{-3})[b]	$\Delta\chi_m$ (g^{-1})[b]
(1.0)	0.691	—	—
0.998	0.640	0.078	0.076
0.995	0.634	0.084	0.082
0.990	0.630	0.090	0.087
0.985	0.627	0.095	0.092
0.980	0.625	0.100	0.097
0.975	0.623	0.105	0.102
0.970	0.621	0.109	0.105
0.960	0.618	0.117	0.113
0.950	0.616	0.124	0.119
0.940	0.614	0.130	0.125
0.930	0.612	0.136	0.130
0.920	0.610	0.141	
0.910	0.608	0.146	
0.900	0.607	0.151	
0.860	0.600	0.169	(0.159)[c]

[a] Volume susceptibilities, corrected for thermal expansion of the reference liquids, have an estimated absolute uncertainty of ± 1.5%. The precision is ⩽ 1%.

[b] Values are taken from the smooth curve fit to the data. The standard deviation of the data from the curve is 0.004×10^{-6}.

[c] Estimated value based upon linear extrapolation of the $\rho(T)$ data.

Figure 3 shows the density of MBBA over the range 20 to 65°C. We find that the data are represented, on each side of the transition temperature, by straight lines within the uncertainty of the measurement. A value of $-8.2 \pm 0.1 \times 10^{-4}$ g cm^{-3} °C^{-1} for $d\rho/dT$ is obtained. Pretransitional effects are seen at $\sim T_c-4°$ but are neglected here. The volume increase obtained upon passing from the nematic to the isotropic phase is 0.19%. The value of $d\rho/dT$ for acetone[9] is -1.11×10^{-3} g cm^{-3} °C^{-1} and our measurements on 1,4-dioxane gave $d\rho/dT = -1.13 \times 10^{-3}$ g cm^{-3} °C^{-1}. No previous literature values for the thermal coefficients could be found for either MBBA or 1,4-dioxane.

In the absence of long-range order effects, we expect that χ possesses no temperature dependence in the isotropic phase ($T > 46$°C) other than from density changes. Figure 2 shows that $\Delta H/H_0$ *increases* in a linear fashion from density changes above the nematic–isotropic transition. Assuming that the density changes can be well approximated by a linear expression[9] for the liquids in the temperature range studied, we expect that the slope of the data curve for $T > 46$°C indicates the effect of the specific volume changes that one must compensate for (when $T < 46$°C) before applying Eq. (2). The following equation, which gives a linear dependence of $\Delta H/H_0$ on the temperature, can be derived from Eq. (1):

$$\frac{\Delta H_{T'} - \Delta H_T}{H_0} = (A\chi_1\alpha_1 + B\chi_2\alpha_2)(T' - T) \qquad (3)$$

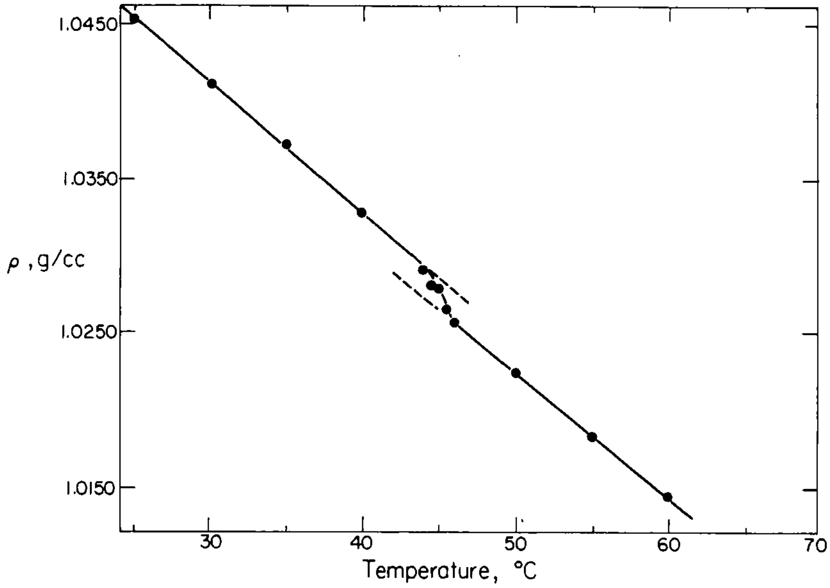

FIGURE 3. Density of MBBA vs. temperature.

where $\alpha = d\rho/dT$, A and B are cell constants, and χ_1 and χ_2 are the mass suspectibilities of the sample and reference liquid, respectively.

The values of $d\rho/dT$ given above, used with Eq. (3), gave the linear correction shown as broken lines in Figure 2a and b. The correction line does indeed fit the data for $T > T_c$ as anticipated. The corrected values of $\Delta\kappa$ at each temperature are then calculated with Eq. (2) using $(\Delta H_{\text{nem}} - \Delta H_{\text{iso}})/H_0$, measured to the broken line. Table I gives the values of $\Delta\kappa$ as well as the corresponding values of $\Delta\chi$ (both in cgs units).

DISCUSSION

Since the order of the nematic phase is far from complete at attainable temperatures,[10] the anisotropy of measured susceptibility, $\Delta\chi_m$, is in fact less than the anisotropy, $\Delta\chi_a$, of the molecular susceptibility tensor. These anisotropies are related[8,10] by

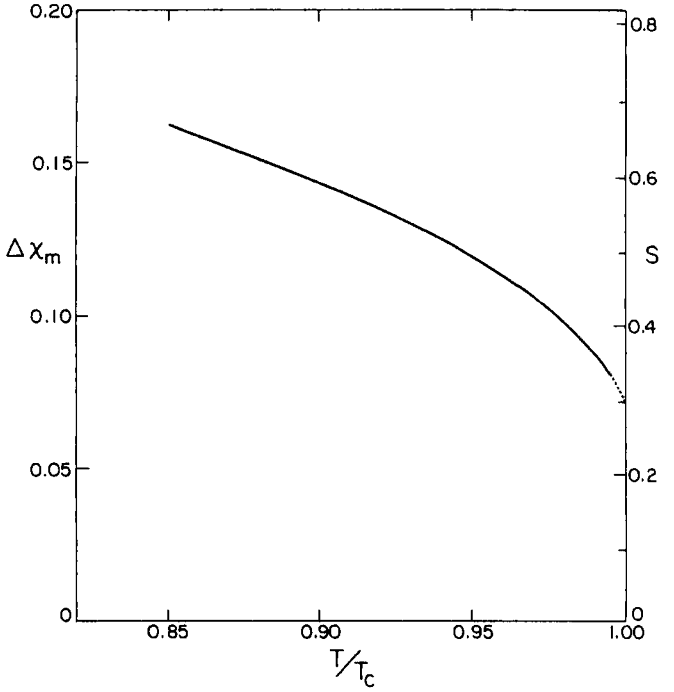

FIGURE 4. $\Delta\chi_m$ as a function of the reduced temperature. The S ordinate on the right side is obtained by assuming $\Delta\chi_a = 0.24$.

$$\Delta\chi_m = S\Delta\chi_a \tag{4}$$

where

$$S = 3/2 < \cos^2\theta - 1/3 > \tag{5}$$

θ being the angle between the director (magnetic-field direction) and the *minor* principal axis of diamagnetic susceptibility. The latter, assuming cylindrical symmetry, coincides with the long molecular axis. Thus, variation of $\Delta\chi_m$ itself shows the relative dependence of the order parameter, S, upon temperature. If $\Delta\chi_a$ is known, then S can be obtained. Figure 4 shows our values of $\Delta\chi_m$ for MBBA plotted as a function of reduced absolute temperature, T/T_c.

Although our data do not lead directly to values of S since $\Delta\chi_a$ is not known for MBBA, we note that the temperature variation of $\Delta\chi_m$ is different from that predicted from the theory of Maier and Saupe,[11] and shows that a greater than expected rate of change in the nematic order takes place in the reduced temperature range of 0.86 to 1.0. A further important consequence of the Maier-Saupe theory is that for *all* nematics, the value of S at the transition temperatures, S_c, is ~ 0.44.[11] Our data for MBBA indicate that if such were the case, then S would reach unity by a reduced temperature of ~ 0.80. Since that would be physically unrealistic, we conclude that S_c must be significantly less than 0.44 for MBBA, a situation that can result according to Chandrasekhar's recent modification[12,13] of the mean-field theory.

If, as an approximation of $\Delta\chi_a$ for MBBA, we use the *p*-azoxyanisole, PAA, value† of 0.242,[1] the right-hand ordinate of Figure 4 is obtained, giving $S_c \sim 0.3$. An S_c value ~ 0.33 is obtained for PAA by Chandrasekhar's theory, and a similar value can be estimated from the PAA susceptibility data of Gasparoux and coworkers.[8]

The point to be emphasized is that our MBBA results are consistent with other evidence that S_c values for nematic liquids may have values covering a fairly wide range, so far, at least from 0.3 to 0.5.[13] The value of S_c for a particular nematic phase appears to depend upon the relative contributions of the attractive and repulsive terms in the potential energy expression used in the extended mean-field theory.[13] The dependence of these terms upon the molecular structure is not yet clear.

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† We assume here that $\Delta\chi_a$ will be similar for MBBA and PAA, each of which possess a *trans* arrangement of phenyl groups about a central double bond. The main source of diamagnetic anisotropy from these compounds is expected to arise from the aromatic rings and central linkage.[2] Data from a number of polynuclear (nonfused ring) aromatic compounds[2] show that an additive relation holds to within ~ 10%.

While this study was in progress, values of $\Delta\chi_m$ vs. T for MBBA were published[8] that are in poor agreement with those from our NMR measurements. The discrepancies are attributed[14] to the questionable purity of the MBBA sample used in the earlier work[8] and improved values have appeared since this work was complete.[15] Also, since the completion of the present work, a paper[16] has appeared which uses $\Delta\kappa$ values for MBBA that were determined by an unspecified method. Our results appear to agree within ~ 5%of these values, but comparison is difficult since the diamagnetic anisotropy was not explicitly given.[16]

SUMMARY

Nuclear magnetic resonance offers an attractive means for determining the value of the diamagnetic susceptibility and anisotropy of liquid crystals because standard high-resolution NMR equipment can be used. A possible disadvantage of the NMR method, compared with the more conventional methods, is the need to correct for the specific volume changes that, in variable-temperature studies, both the liquid crystal and a reference liquid undergo. In the case of MBBA and the reference liquids acetone and dioxane, it is shown that the correction is straightforward since the various thermal coefficients of expansion are known and can be assumed linear.

The temperature variation of the diamagnetic anisotropy for nematic MBBA was found to disagree with that expected on the basis of Maier-Saupe theory. A value for $S_c \approx 0.3$ is estimated from the data and is compatible with the result of more recent theory.[12,13] A more precise value of S_c for MBBA by susceptibility measurements must await the determination of $\Delta\chi_a$.

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